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BLACK-CHROME SOLAR-SELECTIVE COATINGS
ELECTRODEPOSITED ON METALLIZED-GLASS TUBES*

by

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ABSTRACT

Glass tubes, initially metallized with thin layers of chromium and copper, were electroplated with copper and black chrome. The optical properties of the black-chrome-plated tubes were excellent with $\alpha_s = 0.94$ and $\epsilon_{TH}(25^\circ\text{C}) = 0.08$. Thermal-cycling tests of the tubes revealed relatively stable optical properties until temperatures around 400°C in vacuum were reached.

1. Introduction

Commercially available evacuated tubular collectors (ETCs)^{1,2} are typically of all-glass dewar-type construction. The outside surface of the inner glass tube is coated with a solar-selective absorber film, typically vapor deposited in a batch-mode vacuum coater. These selective absorber coatings have solar absorptivities α_s in the range 0.75 to 0.85, and emissivities $\epsilon_{TH}(25^\circ\text{C})$ in the range 0.05 to 0.08.

Because solar absorptivities above 0.9 can (and should) be obtained for a solar-selective absorber, and because a less expensive method than batch-mode vapor-deposition would be desirable, an electroplated black-chrome coating on glass tubes was tried in these experiments. Electroplated black-chrome is the current favorite among selective coatings because of its durability in high humidity and at temperatures up to 350°C and good optical properties.

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($0.92 \leq \alpha_s \leq 0.96$ and $0.08 \leq \epsilon_{TH} (25^\circ\text{C}) \leq 0.12$). At the temperatures and concentration ratios where ETCs are likely to be used, gains in α_s are favored over equivalent increases in ϵ_{TH} .³ This means that increasing α_s from 0.85 to 0.95 at the expense of increasing ϵ_{TH} from 0.05 to 0.15 would result in an overall performance gain. The high values of α_s consistently obtained with electroplated black chrome suggested its use in these experiments. In fact, values of $\alpha_s = 0.94$ and $\epsilon_{TH} (25^\circ\text{C}) = 0.08$ were obtained, representing an increase in α_s of 0.09 for an increase in ϵ_{TH} of only 0.03 from those commercial ETCs having the highest absorptivities.

Following sections of this paper will describe the experimental procedure for electroplating black-chrome on glass tubes, the optical and thermal-cycling tests, and a discussion of the results.

2. Experimental Procedure

There are two basic methods to electrodeposit coatings on glass. One method is the electroless process⁴ whereby nickel or copper is deposited directly on an etched glass surface. The other method is to premetallize the glass surface before plating so that the surfaces to be coated can conduct the electroplating current. The second, and far more common method was chosen here.

For convenience, the initial metallized layer was vacuum-deposited. However, there are non-vacuum techniques for premetallizing glass. One method uses brush, dip, or spray-on organometallic films.⁵ Such films of a precious-metal type (Engelhard Liquid Bright Gold, A-3654) were tried and were subsequently successfully copper-plated. However, these films exhibited unacceptable adhesion strength (a precious metal resin was chosen for this "proof of concept" demonstration because these resins reduce to a pure metal when fired in air). The lack of adhesion to the substrate resulted in discontinuing this present organometallic film work for the more successful vacuum evaporated coatings.

Standard 1/8 in Pyrex tubing stock was used as the glass substrate in these experiments. After cleaning, a 0.05- μm -thick layer of chromium was vacuum deposited on the glass tubes. Next, a 1- μm -thick layer of copper was deposited without breaking vacuum. Two tubes were coated in this manner. The 0.05- μm

chromium and thin copper coatings were deposited, respectively, for adhesion to the glass and to serve as a base for the subsequent electroplated copper.

Next, bright-acid copper was plated onto the vacuum-metallized tubes. Plating was started at a very low current density of around 60 A/m^2 . After about 15 min, the current was increased to the normal current density of about 325 A/m^2 . Approximately 0.005 cm of copper was electroplated. This thick copper layer was plated to carry the heavy currents needed to electroplate black chrome.

The copper-plated tubes were electroplated with black chrome using a Chrom-Onyx plating bath⁶ at Sandia Laboratories, Albuquerque, NM. A successful black chrome electroplate was obtained with a current density of 840 A/m^2 for a plating time of 8-3/4 min. The two copper-plated tubes were black chrome electroplated, and subsequently used in the optical and thermal-cycling testing. Several pieces of 0.0063 cm (0.0025 in.) thick copper foil were also black chrome plated at Sandia in the same bath, as reference coatings for the sample testing.

3. Optical and Thermal Cycling Testing

The solar reflectivity $R_s (= 1 - \alpha_s)$ of the samples was measured with a Gier-Dunkle MS-251 Solar Reflectometer, and the infrared reflectivity $R_{TH} (25^\circ\text{C}) (= 1 - \epsilon_{TH} (25^\circ\text{C}))$ was measured with a Gier-Dunkle DB-100 Infrared Reflectometer. Optical measurements were made on various black chrome coatings, including the Sandia copper foil, Berry Solar foil (copper, also),⁷ and the tubes.

The Gier-Dunkle instruments are designed to give values of α_s and $\epsilon_{TH} (25^\circ\text{C})$ for flat surfaces, integrated over the solar and 25°C black-body spectrum, respectively. A sample holder was machined from Bakelite in order to measure the values of α_s and $\epsilon_{TH} (25^\circ\text{C})$ for the round tubes. This sample holder was fabricated with one side flat and the opposite side curved. A viewing port was machined through the sample holder from the flat to the curved side. The curved side made a light-tight seal against the tube so that the instruments measured, through their viewing ports, reflectivities of a round portion of a tube.

In order to calibrate the optical properties of round absorber surfaces against similar flat surfaces, pieces of absorber foil were measured as flat surfaces, and also as curved surfaces by wrapping the foil around uncoated 28 mm glass tubes, and placing the foil-covered tube into the curved sample holder. (There is an implicit assumption here that the angular distribution of the optical properties is the same for the curved foil and the coated glass tubes.) In Table I, typical measurements on the flat and curved foils are given, as well as those for the tubes before thermal-cycling tests were begun. Note that the values of R_s and R_{TH} (25°C) in Table I are reasonably consistent when comparing the two curved surfaces. The average ratio of flat foil R_s values to curved foil R_s values is 1.30. The average ratio of flat foil R_{TH} (25°C) values to curved foil R_{TH} (25°C) values is 1.24. These ratios, measured for the foil whenever R_s and R_{TH} (25°C) values were measured for the tubes, were used as a calibration to determine the values of ϵ_s and ϵ_{TH} (25°C) for the curved tubes. Applying these ratio corrections to the R_s and R_{TH} (25°C) values for the black-chromed tubes, we can summarize the results in Table II. These values of ϵ_s and ϵ_{TH} (25°C) in Table II (equal to 0.94 and 0.08, respectively, for both tubes) can be taken as a baseline for the thermal-cycling experiments.

TABLE I

Comparison of solar and infrared reflectivities, R_s and R_{TH} (25°C), respectively, for flat and curved black chrome coatings.

<u>Absorber</u>	<u>R_s</u>	<u>R_{TH} (25°C)</u>
1. Sandia foil, flat	0.05	0.89
2. Sandia foil, curved	0.04	0.72
3. Berry foil, flat	0.08	0.93
4. Berry foil, curved	0.06	0.75
5. Tube No. 1	0.05	0.74
6. Tube No. 2	0.05	0.73

TABLE II

Measured values of α_s and ϵ_{TH} (25°C) corrected for tubular geometry, for various black-chrome selective absorbers.

Absorber	α_s	ϵ_{TH} (25°C)
1. Sandia foil	0.95	0.11
2. Berry foil	0.92	0.07
3. Tube No. 1	0.94	0.08
4. Tube No. 2	0.94	0.08

The thermal-cycling tests consisted of placing the two black-chrome plated glass tubes and a piece of Berry foil into a vacuum baking system for a period of time. The optical properties (α_s , ϵ_{TH} (25°C)) were then measured after each thermal cycling, at progressively higher temperatures.

The foil and glass tube samples were vacuum-baked at 4×10^{-5} torr in a quartz-tube furnace chamber. The samples were baked at 100°C, 200°C, 250°C, 300°C, 350°C, and 400°C for times ranging from 47 hs to 165 hs. Significant changes in α_s did not occur for the electroplated tubes until the baking temperature reached the 400°C range. After 165 hs at 400°C, Tube No. 1 α_s decreased from the original value of 0.94 to 0.74; Tube No. 2 α_s decreased from an original value of 0.94 to 0.81. The foil α_s also decreased after baking in the 400°C range, from an original value of 0.92 to 0.88. The emissivities ϵ_{TH} (25°C) of both the tubes and the Berry foil were little affected by the baking process (accuracy for the Gier-Dunkle instruments is estimated $\pm 1.5\%$). It should be noted here that Tube No. 1, which showed a larger degradation in α_s than did Tube No. 2, had displayed a rougher, pitted surface after copper electroplating than did the surface of Tube No. 2.

4. Discussion

Tube coating samples were analyzed in an effort to understand why α_s degraded at 400°C temperatures. These coatings adhered so tightly to the glass (due primarily to the initial vapor-deposited chromium layer) that small coating samples could not be peeled from the glass. Coated glass-substrate

sample pieces were removed from the tubes with a glass-cutting saw. The samples (from Tube No. 1 with the rough surface and No. 2 with the smooth surface) were examined by ion and electron microprobes. Both samples yielded essentially identical results.

Mass scans on the surfaces of the samples detected the following elements: H, Li, B, C, O, F, Na, Mg, Al, Si, Cl, K, Ca, Pb, and Cu. All responses, except for copper, were of low level, and decreased with sputtering depth. It was concluded that the noncopper elements were present in surface contamination. The strength of the copper signal obtained from the surface of the selective coating was approximately 20% of that from pure copper. The possibility exists that the copper signal obtained when examining the surface of the black chrome layer could have resulted from porosity in the layer, which would expose small regions of the underlying copper. This was particularly suspected for the pitted surface of Tube No. 1. However, two-dimensional ion images for copper on the surface did not show any localized high concentration of copper as would be expected from a porous coating.

One-dimensional scans made by the electron microprobe over the edge of metallographically polished cross-sections of both samples produced results typified by those shown in Fig. 1. These results are suggestive of penetration of the black chrome layer by copper, but not of the reverse. The layer, less than one micrometer in thickness, is too thin for more accurate analysis by electron microprobe.

Thermodynamic calculations show that copper will not reduce Cr_2O_3 . For penetration of copper by chromium, it seems essential that some of the Cr_2O_3 would have to be reduced to chromium. These considerations lend credence to the indications that copper has penetrated the black chrome layer, but not the reverse. Presumably, the rougher coating on Tube No. 1 is slightly thinner, and less uniform, than the coating on Tube No. 2, allowing faster penetration of the black chrome layer by diffusing copper atoms. A sample of unbaked, black-chrome-plated Sandia copper foil was also examined by both the electron and ion microprobes. As a result of these examinations, it was concluded that no detectable copper diffusion had taken place in the unbaked foil.

As mentioned, the black-chrome Berry foil did not show as noticeable a decrease in ϵ_g ($\Delta\epsilon_g = -0.04$) as did the tubes ($\Delta\epsilon_g = -0.20$). The reason

for this is apparently a 0.005 cm (0.002 in.) layer of nickel electrodeposited on the copper before the black chrome.⁹ The nickel acts as a barrier to diffusion of copper atoms into the electroplated black chrome, and, hence, retards degradation of α_s .⁹ Inclusion of a nickel layer on the glass tubes would likewise retard degradation of their α_s values.

It is interesting to note that diffusion of copper atoms into physical vapor deposited (PVD) black chrome does not appear to be a problem,¹⁰ as it is with electroplated black chrome. It can be hypothesized that electroplated black chrome has a more open structure than PVD black chrome that allows diffusion through interstitial voids.

5. Summary and Conclusions

Glass tubes were PVD coated with thin layers of chromium and copper, before electrodeposition of copper and black chrome. The initial optical properties of the black-chrome-plated tubes were excellent ($\alpha_s \approx 0.94$, ϵ_{TH} (25°C) ≈ 0.08). Thermal-cycling tests of the tubes revealed relatively stable optical properties until temperatures around 400°C in vacuum were reached. Inclusion of an electroplated layer of nickel between the layers of copper and black chrome would retard diffusion of copper atoms into the black chrome layer and, hence, retard degradation of α_s for the tubes at temperatures 400°C in vacuum.

Present ETC absorber surfaces have $\alpha_s \sim 0.85$, ϵ_{TH} (25°C) ~ 0.05 . The use of glass tubes electrodeposited with black chrome would raise α_s to 0.94 without increasing ϵ_{TH} (25°C) above 0.08.

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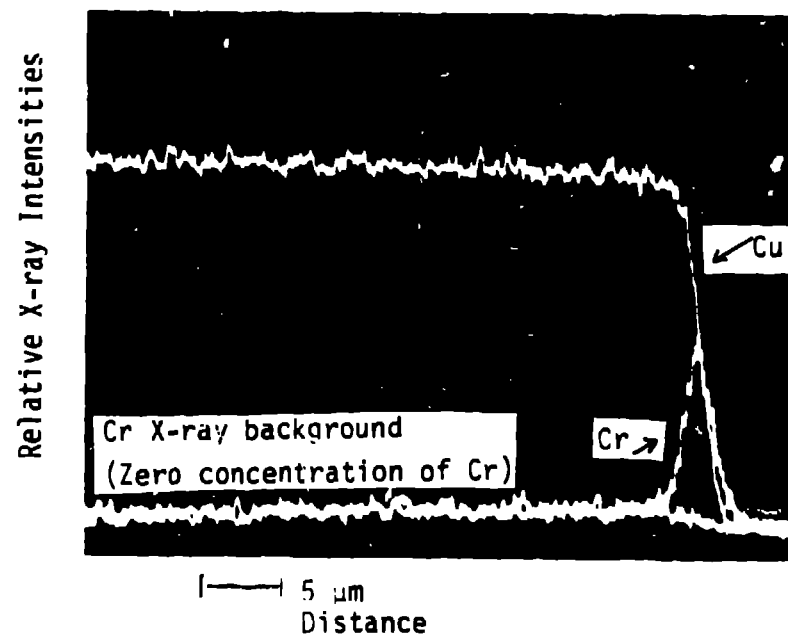


Fig. 1.
One-dimensional distributions of Cu and Cr across
Cu substrate and black chrome coating
on glass tubes.

7. References

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